TITLE: Heat of Dissolution Measurements for CO_2 in Mixed Alkanolamine Solvents

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PRINCIPAL AUTHOR: Vinayak N. Kabadi

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SUBMITTING INSTITUTION: North Carolina A&T State University
1601 East Market Street
Greensboro, NC 27411

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ABSTRACT

The main objective of this project is to measure heat of dissolution of CO_2 in carefully selected mixed alkanolamine solvent systems, and provide such directly measured data that might be used for efficient design of CO_2 capture processes, or for better understanding of thermodynamics of CO_2- alkanolamine systems. Carbon dioxide is one of the major greenhouse gases, and the need for stabilization of its composition in earth's atmosphere is vital for the future of mankind. Although technologies are available for capture and storage of CO_2, these technologies are far too expensive for economical commercialization. Reduction of cost would require research for refinement of the technology. For more economical CO_2 capture and regeneration, there is a need for development of more efficient solvent systems. In this project we will extend the thermodynamic database by measuring heat of solution data of CO_2 in mixed solvents made of MEA (monoethanolamine), MDEA (methyldiethanolamine), piperazine, and water. Mixed solvents of different compositions will be selected and in each case data will be measured at temperatures 40 and 80C and various partial pressures of CO_2. At the end of the project, observations, conclusions, and recommendations will be derived for the choice of mixed solvents for efficient CO_2 capture with potential for commercialization.

EXECUTIVE SUMMARY

The main objective of this project is to measure heat of dissolution of CO_2 in carefully selected mixed alkanolamine solvent systems, and provide such directly measured data that might be used for efficient design of CO_2 capture processes, or for better understanding of thermodynamics of CO_2- alkanolamine systems. Carbon dioxide is one of the major greenhouse gases, and the need for stabilization of its composition in earth's atmosphere is vital for the future of mankind. Although technologies are available for capture and storage of CO_2, these technologies are far too expensive for economical commercialization. Reduction of cost would require research for refinement of the technology. For more economical CO_2 capture and regeneration, there is a need for development of more efficient solvent systems. In this project we will extend the thermodynamic database by measuring heat of solution data of CO_2 in mixed solvents made of MEA (monoethanolamine), MDEA (methyldiethanolamine), piperazine, and water. Mixed solvents of different compositions will be selected and in each case data will be measured at temperatures 15, 40 and 80C and various partial pressures of CO_2. At the end of the project, observations, conclusions, and recommendations will be derived for the choice of mixed solvents for efficient CO_2 capture with potential for commercialization.

Data measurements for CO_2 in aqueous MEA, MDEA and mixtures of MEA and MDEA and piperazine were completed and reported previously. During the current period of performance, preliminary data measurements for CO_2 in aqueous mixtures of MDEA and an inorganic salt potassium fluoride ($KF.2H_2O$) were completed. The goal of these measurements was to investigate whether potassium fluoride enhances the solvent properties of MDEA. Results do not show any obvious improvements. The data showed no appreciable improvements in solvent properties as a result of adding potassium fluoride.

Efforts are continuing to analyze and write up all the data measured into journal publications. Two papers are currently in preparation. The first paper includes all the measured data for pure and mixed solvents. In the second paper the data are regressed to present simple correlations for solubility of CO_2 in these solvents. An analysis is also presented of the heat of solution of CO_2 in aqueous alkanolamine solvents. All this work will be described in the final technical report on the project.

TABLE OF CONTENTS

1. Introduction

Carbon dioxide is one of the major greenhouse gases, and the need for stabilization of its composition in earth's atmosphere is vital for the future of mankind. Although technologies are available for capture and storage of CO_2, these technologies are far too expensive for economical commercialization. Reduction of cost would require research for refinement of the technology. The idea of capturing CO_2 from the flue gas of power plants did not start with concern about the greenhouse effect. Rather, it gained attention as a possible economic source of CO_2 , especially for use in enhanced oil recovery operations where CO_2 is injected into oil reservoirs to increase the mobility of the oil and, therefore, the productivity of the reservoir. Several commercial CO_2 capture plants were constructed in the late 1970s and early 1980s in the US. The North American Chemical Plant in Trona, CA, which uses the carbonation of brine to produce CO_2 , started operation in 1978 and is still operating today. However, when the price of oil dropped in mid-1980s, the recovered CO_2 was too expensive for enhanced oil recovery operations and all of the other CO_2 capture plants were closed.

Historically, CO_2 capture processes have required significant amounts of energy, which reduces the power plant's net power output. For example, the output of a 500 MW (net) coal-fired power plant may be reduced to 400 MW (net) after CO_2 capture. This imposes an "energy penalty" of 20%. The energy penalties of current capture technologies range from about 30% for conventional coal to about 15% for advanced coal. It is desired that in the next decade these numbers be brought to 50% of their current values.

To date, all commercial CO_2 capture plants use processes based on chemical absorption with the monoethanolamine (MEA) solvent. MEA was developed over 60 years ago as a general, non-selective solvent to remove acid gases, such as CO_2 and H_2S, from natural gas streams. The process was modified to incorporate inhibitors to resist solvent degradation and equipment corrosion when applied to CO_2 capture from flue gas. Also, the solvent strength was kept relatively low, resulting in large equipment sizes and high regeneration energy requirements. The process allowed flue gas to contact an MEA solution in the absorber. The MEA selectively absorbed the CO_2 and was then sent to a stripper. In the stripper, the CO_2 –rich MEA solution was heated to release almost pure CO_2 . The lean MEA solution was then recycled to the absorber.

Other processes have been considered to capture CO_2 from the flue gas of a power plant, e.g., membrane separation, cryogenic fractionation, and adsorption using molecular sieves. These processes are even less efficient and more expensive than the chemical absorption. The reason can be attributed to the very low CO_2 partial pressure in the flue gas. Therefore, a high priority research need is to formulate new solvents that can significantly reduce the energy penalty associated with chemical absorption. The new solvents must increase the loading (amount of CO_2 dissolved per unit amount of solvent), and the rate of CO_2 dissolution while maintaining a low heat of solution, so as to minimize the energy requirements during the solvent regeneration.

For the processes based on the absorption of CO_2 by aqueous alkanolamines, the energy penalty or the cost of the process depends mostly on three factors: (1) the loading of CO_2 (moles of CO_2 absorbed per mole of amine), (2) the rate of CO_2 absorption, and (3) the energy requirement for the release of CO_2 in the stripper. For a number of solvents, detailed studies are available in the literature for the first two factors. Aqueous MEA solvents suffer from the limitation that CO_2 loading cannot exceed much higher than 0.5. An amine that is considered as a potential replacement for MEA is methyldiethanolamine (MDEA) because of the high loading of CO_2 (approaching 1) which is attributed to the stoichiometry of the reaction forming carbamate. However, the rate of CO_2 absorption by MDEA is too low for commercial applications. Mixed solvents containing MEA and MDEA, and diethanolamine (DEA) and MDEA in water seem to provide good solutions to give high absorption rates as well as CO_2 loading. Recently researchers have also started looking at other additives to aqueous MEA and MDEA mixtures to enhance solubility and rate of absorption of CO_2. These include sulfolane, N-methylpyrrolidone (NMP), and piperazine (PZ). Of these, piperazine seems to be the most effective in increasing the solubility of CO_2. The data available in the literature indicate that aqueous mixtures of MEA, MDEA and piperazine have potential to provide a solvent system superior to aqueous MEA solvent of the current commercial capture plants. However, a true determination of this is difficult without a detailed study of the relative energy requirements for each of the solvents. Such a study is not available in the literature, mostly because of lack of experimental data on the heats of dissolution of CO_2 in the aqueous alkanolamine solvents. Data are available only for a few systems and at limited conditions.

For more economical CO_2 capture and regeneration, there is a need for development of more efficient solvent systems. In this project we will extend the thermodynamic database by measuring heat of solution data of CO_2 in mixed solvents made of MEA (monoethanolamine), MDEA (methyldiethanolamine), piperazine, and water. Mixed solvents of different compositions will be selected and in each case data will be measured at a few temperatures and at different concentrations of the aqueous solutions. At the end of the project, observations, conclusions, and recommendations will be derived for the choice of mixed solvents for efficient CO_2 capture with potential for commercialization.

2. Progress of Experimental Measurements

In this report we present the solubility and enthalpy data measured for CO_2 in aqueous MDEA-potassium fluoride mixtures. Data were measured for CO_2 in aqueous MDEA+KF.2H_2O mixture containing 30 wt% MDEA and 8 wt% KF.2H_2O at three temperatures, 15 C, 40 C, and 75 C, . The procedure for data measurements was the same as described in previous reports. The results for solubility (expressed as loading factor α which is defined as moles of CO_2 dissolved per mole of amine+potassium fluoride and enthalpy are summarized in Table 1. Detailed data are listed in Tables 2 to 4. For data conversion from volume to molar units, density of aqueous MDEA-potassium fluoride

solution is needed. Density of 30-8 wt% MDEA-KF.2H_2O solution at 20 C was measured in the laboratory as 1.058 g/ml. Figure 1 shows a comparison of loading of CO_2 in 30 wt% MDEA solution, 30+10 wt% MDEA+PZ mixture and 30+8 wt% MDEA+KF.2H_2O mixture, all at 40 C. Compared to MDEA, MDEA+PZ seems to increase the loading of CO_2 somewhat, however loading of CO_2 actually decreases upon addition of potassium fluoride. Figures 2 to 4 show the data for 30+8 wt% MDEA+KF.2H_2O mixture at 15, 40 and 75 C. Comparison of the data with aqueous MDEA (30 wt%) solvent at 15 and 75 C also shows that the addition of potassium fluoride results in decrease in CO_2 loading also at these temperatures. It was therefore concluded that potassium fluoride does not enhance the solvent properties of aqueous alkanolamines.

3. Data Analysis and Other Current Work

An observation our heat of solution data indicate that the heat of solution per mole of CO_2 is fairly constant with CO_2 loading at low CO_2 concentrations, but it decreases closer to the saturation concentration. Attempts are continuing to model this behavior, and obtain expressions for heats of mixing as function of CO_2 concentration. The results will be presented in the final report.

Efforts are continuing to analyze and write up all the data measured into journal publications. Two papers are currently in preparation that include our solubility and enthalpy data for CO_2 in aqueous MEA and MDEA solutions, a compilation of all literature data for these systems, and correlations for CO_2 solubility and enthalpy as a function of temperature pressure and amine concentration. The objective is to provide data correlations that will be very useful in optimizing design of CO_2 removal processes. All the results and the contents of the two papers will be described in the final technical report.

4. Conclusions and Plans for the Final Technical Report

All the efforts now are on completing two papers to be submitted for publication in Industrial & Engineering Chemistry Research, and preparing and submitting the final technical report by June 30.

Table 1: Solubility and Enthalpy data for CO_2 in aqueous MDEA+KF mixed solvent

MDEA+KF solution				
Temp ^{0}C	*MDEA+KF Wt %*	*Solubility, α mol CO2/mol amine*	*kJ / mol CO_2*	*kJ / mol Amine*
15	*30+0*	*1.26*	*-39*	*-49*
	30+8	*0.927*	*-33.2*	*-35.1*
40	*30+0*	*1.17*	*-43.2*	*-50.2*
	30+8	*0.86*	*-42*	*-36*
75	*30+0*	*0.82*	*-52.8*	*-43.2*
	30+8	*0.735*	*-52*	*-38.5*

Table 2: Data for (30-8) wt% mixture of MDEA+KF at 15 C

CO_2 (sccm)	CO_2 mol/S	MDEA-KF (ml/min)	MDEA-KF (mol/S)	Loading	Avg ΔH	ΔH (KJ/mol CO_2)	ΔH (KJ/mol MDEA-KF)
0.2	1.468E-07	0.035	2.07779E-06	0.07064	-6.35	-43.262	-3.056
0.3	2.202E-07	0.035	2.07779E-06	0.10596	-9.55	-43.376	-4.596
0.6	4.403E-07	0.035	2.07779E-06	0.21193	-19.1	-43.376	-9.192
1	7.339E-07	0.035	2.07779E-06	0.35321	-31.85	-43.398	-15.329
1.5	1.101E-06	0.035	2.07779E-06	0.52982	-47.8	-43.421	-23.005
2.2	1.615E-06	0.035	2.07779E-06	0.77707	-68	-42.116	-32.727
1.5	1.101E-06	0.02	1.18731E-06	0.92718	-41.4	-37.607	-34.869
3	2.202E-06	0.035	2.07779E-06	1.05963	-73	-33.156	-35.133
0.5	3.67E-07	0.004	2.37462E-07	1.5453	-8.35	-22.755	-35.163

Table 3: Data for (30-8) wt% mixture of MDEA+KF at 40 C

CO_2 (sccm)	CO_2 mol/S	MDEA-KF (ml/min)	MDEA-KF (mol/S)	Loading	Avg ΔH	ΔH (KJ/mol CO_2)	ΔH (KJ/mol MDEA-KF)
0.3	2.2E-07	0.032	1.8997E-06	0.1159	-10.9	-49.507	-5.738
0.8	5.9E-07	0.032	1.8997E-06	0.3091	-29	-49.394	-15.266
1.2	8.8E-07	0.032	1.8997E-06	0.4636	-42.6	-48.372	-22.425
1.8	1.3E-06	0.032	1.8997E-06	0.6954	-60	-45.419	-31.584
2.2	1.6E-06	0.032	1.8997E-06	0.8499	-69	-42.736	-36.322
0.76	5.6E-07	0.01	5.9366E-07	0.9395	-21.75	-38.995	-36.637
0.9	6.6E-07	0.01	5.9366E-07	1.1126	-21.8	-33.005	-36.722

Table 4: Data for (30-8) wt% mixture of MDEA+KF at 75 C

CO_2 (sccm)	CO_2 mol/S	MDEA-KF (ml/min)	MDEA-KF (mol/S)	Loading	Avg ΔH	ΔH (KJ/mol CO_2)	ΔH (KJ/mol MDEA-KF)
0.3	2.2E-07	0.032	1.8997E-06	0.1159	-14	-63.587	-7.370
0.8	5.9E-07	0.032	1.8997E-06	0.3091	-37	-63.019	-19.477
1.2	8.8E-07	0.032	1.8997E-06	0.4636	-53.2	-60.408	-28.004
1.8	1.3E-06	0.032	1.8997E-06	0.6954	-71	-53.746	-37.374
0.62	4.6E-07	0.01	5.9366E-07	0.7665	-22.75	-49.998	-38.322
2.2	1.6E-06	0.032	1.8997E-06	0.8499	-73	-45.213	-38.427
0.88	6.5E-07	0.01	5.9366E-07	1.0879	-22.7	-35.148	-38.238

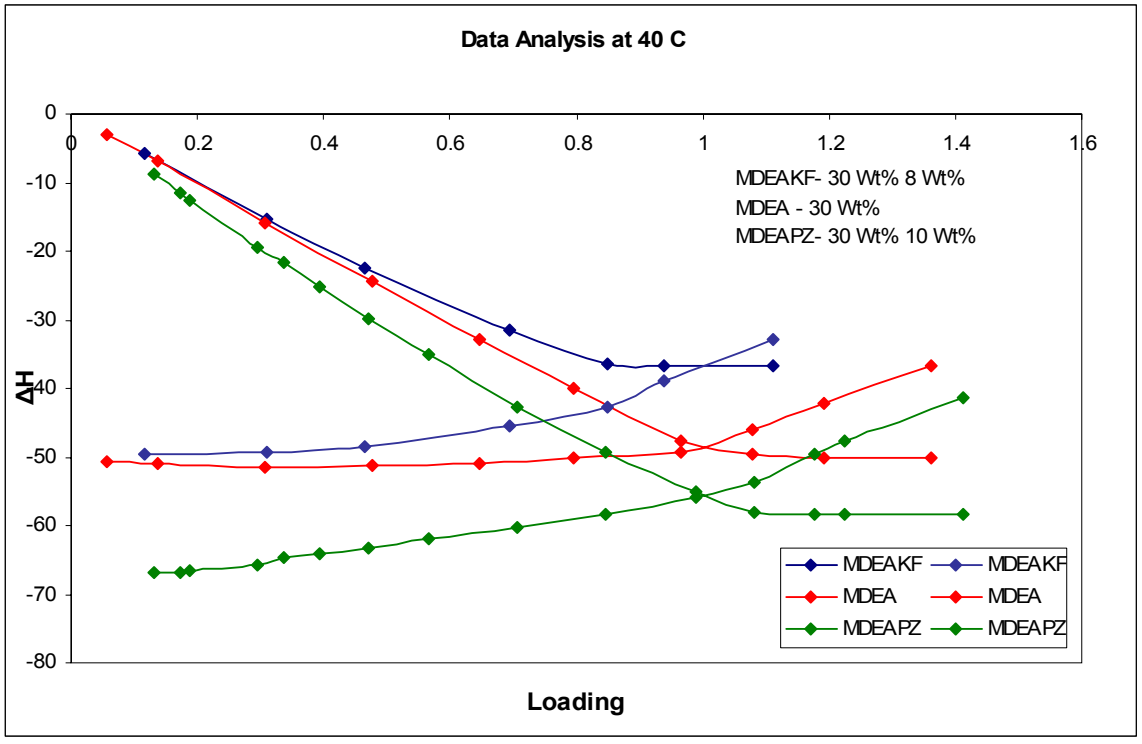

Figure 1: Heat of solution of CO_2 in aqueous MDEA, MDEA-PZ mixture and MDEA-KF mixture at 40 C.

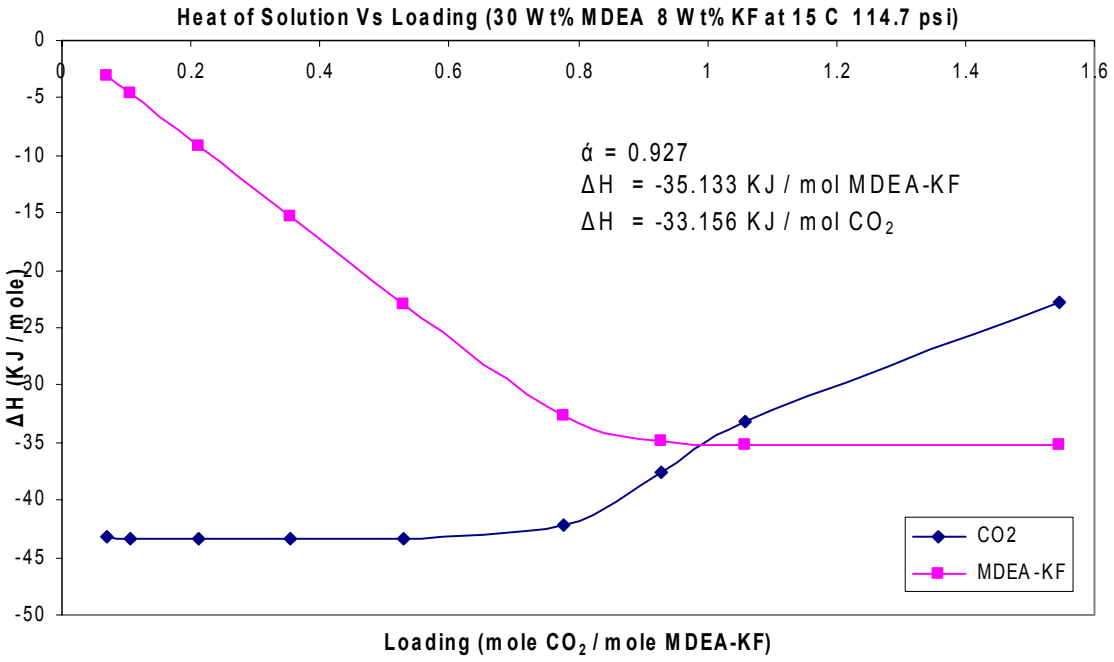

Figure 2: Heat of solution of CO_2 in aqueous MDEA-KF mixture at 15 C.

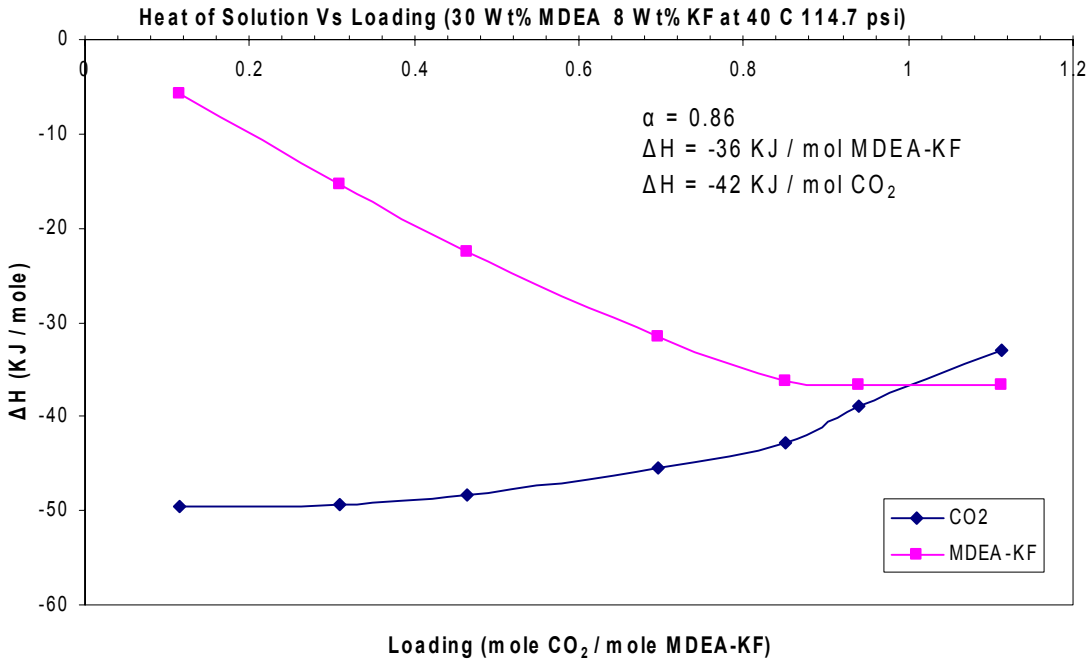

Figure 3: Heat of solution of CO_2 in aqueous MDEA-KF mixture at 40 C.

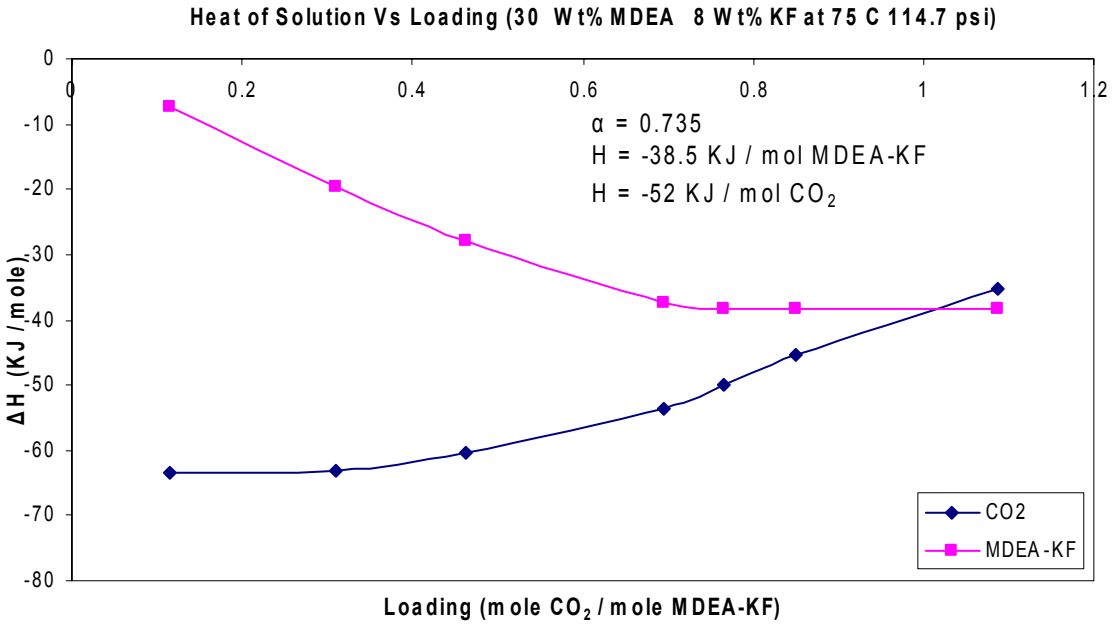

Figure 4: Heat of solution of CO_2 in aqueous MDEA-KF mixture at 75 C.